

Isochroman Structures in Lignin: a New β -1 Pathway

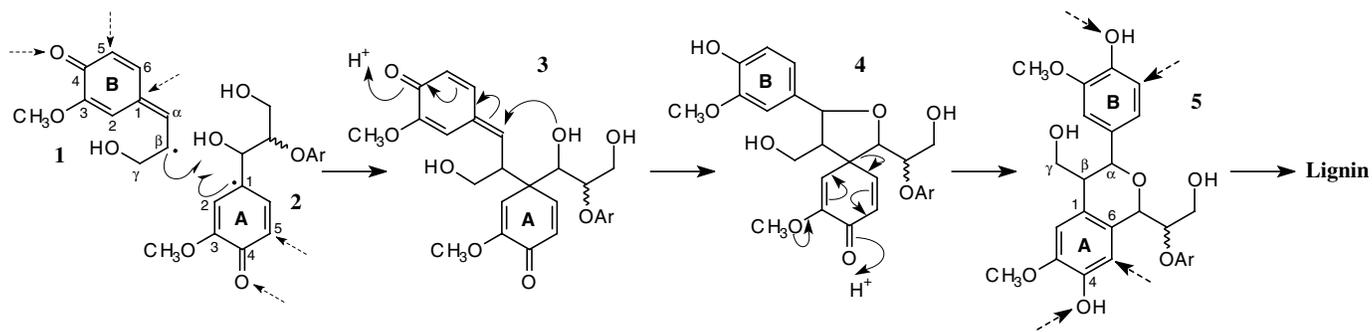
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Abstract: New aryl isochroman structures have been identified in isolated softwood lignins by a combination of diagnostic NMR experiments. Such structural units were recently identified in lignin-derived trimers from wood degraded by the DFRC (derivatization followed by reductive cleavage) method, and have a plausible mechanism for their biosynthesis.

Softwood lignins are produced principally from coniferyl alcohol (4-hydroxy-3-methoxycinnamyl alcohol) via radical coupling reactions.¹⁻³ With four available coupling sites (4-O-, 1-, 5-, and β -) on the monomer radical **1** and at least three (4-O-, 1- and 5-) on subsequent dimers and higher oligomers (e.g. **2**), the resulting polymer is structurally and stereochemically complex. Structural details are still emerging from model studies coupled with NMR, and from closer examination of the products of various degradation methods. Only recently were dibenzodioxocins discovered as important structures in softwood lignins.^{4,5} They have now been found in hardwoods,⁶ grasses and legumes (Brunow, 1997, unpublished; Ralph, 1997, unpublished).

We recently discovered two new aryl isochroman products **5**,⁷ in the trimer fraction of pine wood degraded by the DFRC procedure,^{8,9} that implicated a new pathway following β -1 coupling between a coniferyl alcohol radical **1** and a lignin oligomer radical **2**. The plausible mechanism for biosynthesis of this structural unit, Scheme 1, suggested that it might be found in native lignins. Examining *in situ* lignins with the resolution required to identify such a structure is not possible, but we report here its firm identification in isolated pine lignins.

HMQC or HSQC spectra of various pine milled wood lignin isolates showed a small but diagnostic correlation between δ_C 40.4 and δ_H 3.60 ppm. Regrettably, the other carbon/proton correlations are in congested regions of the spectra but peaks are present at the correct locations. Evidence for the entire proton coupling network was further confirmed by TOCSY experiments, Fig. 1, where correlations corresponding to all four protons on the



Scheme 1. Proposed lignification mechanism in which β -1 coupling of a coniferyl alcohol radical **1** and a preformed lignin oligomer radical **2** produce a quinone methide intermediate **3** which is internally trapped to produce the spiro-compound **4** (rather than fragmenting via the “normal” β -1 pathway¹²). Favored sidechain migration produces the aryl isochroman **5**.⁷ Dashed arrows on **1**, **2** indicate other coupling sites available, and on **5** the potential sites of further radical coupling during lignification.

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aryl isochroman ring are clear [3.60 (β), 4.43 (γ_1), 4.61 (γ_2) and 5.37 (α) ppm]. The correlations represent 5 simultaneous NMR chemical shifts (1 carbon, 4 proton) that correspond exactly with the shifts in the isolated trimer, taedate (as shown on Fig. 1), constituting significant proof. The other isomer isolated following DFRC degradation does not appear at detectable levels in these spectra.

Although the identification of the aryl isochroman structure in isolated milled wood lignins can be made firmly, the apparently low amount visible in spectra does not account for the amounts of derived β -1 products that arise from DFRC-degradation, or various other acidolytic methods. The possibility remains that it is a product of isolation and that a precursor, **4** for example, may be the *in situ* product, as has been proposed.^{10,11} Either way, however, structure **5** provides compelling evidence of the internal cyclization pathway from β -1 intermediate **3**, where no evidence has previously been presented.

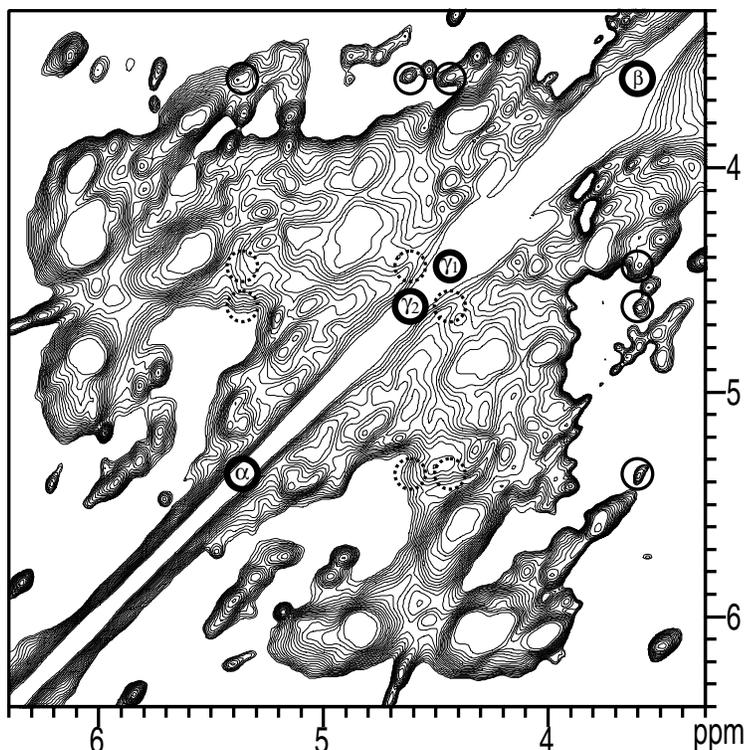


Fig. 1. Sidechain region of a TOCSY (spin lock time, 100 ms) spectrum of *Pinus taeda* acetylated milled wood lignin, clearly showing the H- α /H- β /H- γ_1 /H- γ_2 coupling network. Correlations from the isolated compound **5**, taedate [Ar = (OMe)Ph-CH=CH-CH₂OAc], are at the center of the overlying circles. Other correlations present but not fully resolved are shown with dotted circles. The four ¹H-¹H correlations, along with the diagnostic H _{β} -C _{β} correlation (40.3, 3.60 ppm) in ¹³C-¹H correlation (HMQC or HSQC) spectra, firmly identify the aryl isochroman units **5** in isolated lignins.

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